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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08F 210/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/11098</b> <b>(43) International Publication Date:</b> 27 March 1997 (27.03.97)
<b>(21) International Application Number:</b> PCT/FI96/00494 <b>(22) International Filing Date:</b> 19 September 1996 (19.09.96)  <b>(30) Priority Data:</b> 954475 21 September 1995 (21.09.95) FI  <b>(71) Applicant (for all designated States except US):</b> BOREALIS A/S [FI/FI]; PI 330, FIN-06101 Porvoo (FI).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> LÖFGREN, Barbro [FI/FI]; Niittyranta 17 B, FIN-00930 Helsinki (FI). AALTONEN, Päivi [FI/FI]; Kuhatiehde 1 B 11, FIN-02170 Espoo (FI). KNUUTTILA, Pekka [FI/FI]; Torpparintie 4, FIN-06400 Porvoo (FI).  <b>(74) Agent:</b> FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> OLEFIN POLYMERS WHICH CONTAIN POLAR GROUPS, AND A METHOD FOR THEIR MANUFACTURE  <b>(57) Abstract</b>  An olefin copolymer prepared by polymerizing an olefin which contains 2-5 carbon atoms with a monomer which contains a functional group, the functional monomer being 9-methyl decenoate.		

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Olefin polymers which contain polar groups,  
and a method for their manufacture

5

The invention relates to novel olefin copolymers which contain functional groups and to a method for their manufacture.

10 The linking of monomers which contain functional groups to a hydrocarbon polymer chain signifies the creating of a usable method for the modification of the chemical and physical properties of olefins. By using monomers containing functional groups it is possible to improve properties such as adhesion, dyeability, printability and permeability. Furthermore, a functional group provides a possibility for graft  
15 polymerization and thereby for uses such as compatibilization of blends containing polyolefins.

The Ziegler-Natta catalyst system is commonly used in the polymerization and copolymerization of olefins, but one of the major limitations of these conventional  
20 catalysts is that they are not suited for use in conjunction with monomers containing polar groups. Ziegler-Natta catalysts rather form a complex with the electron pair of a heteroatom, and thus in polymerization they rapidly deactivate the active centers by forming a stable complex with the functional group.

25 The more a polar monomer resembles alpha-olefin, the greater is its potential for becoming polymerized by the same active centers as olefins. The inventors have shown that comonomers which contain heteroatoms can be used for the polymerization of polyolefin. It is known that Lewis acid components (Zr, Al) present in the catalyst tend to form a complex with the unbound electron pairs of  
30 heteroatoms, thus causing deactivation of the catalyst. In practice this non-desirable interaction can be minimized by certain methods, such as (a) by isolating the double bond from the heteroatoms by means of a longer hydrocarbon chain; (b) by adding

a steric barrier around the heteroatom; (c) by decreasing the electron donor character of the heteroatom, for example, by linking to it or in its vicinity a group which attracts electrons; (d) by selecting catalyst components which are inert to functional groups; (e) by precomplexing the functional monomer by using a Lewis acid; or (f)  
5 by using a polar solvent which becomes polarized with the active center but allows the polymerization of the vinyl monomer.

If deactivation can be successfully prevented by one or several of the above-mentioned methods, the copolymerization of functional monomers will become more  
10 popular than it is today.

US patent publication 5,286,800 discloses the polymerization, with alpha-olefins, of comonomers containing functional groups. In these polymerizations there are used borane monomers which are converted, by reactions after the polymerization step,  
15 into polyolefins which contain functional groups.

In Japanese patent publication 61 72 447, the comonomer used is 10-undecen-1-ol which has been pretreated with tri-isobutyl aluminum for 3 hours at room temperature before polymerization.  
20

An object of the present invention is to provide novel copolymers of olefins and monomers containing functional groups. Furthermore, one object of the invention is a method in which the catalyst system has as high an activity as possible in the presence of a polar group. One object of the invention is also to provide for the  
25 copolymerization of olefins a method in which the copolymerization with a polar comonomer takes place in one step, without any pretreatment or postmodification. A further object according to the invention is to provide functional polyolefins in which the molar masses remain relatively high and the molar mass distributions are wide.

30

In the Applicant's previous application *FI 951970*, this object was achieved by using as the functional monomer 2-methyl-3-buten-1-ol, 3-methyl-3-buten-1-ol and 5-hexen-1-ol.

- 5 The olefin copolymer according to the invention, prepared by polymerizing an olefin which contains 2—5 carbon atoms with a monomer which contains a functional group, is characterized in that the functional monomer is 9-methyl decenoate.

The olefin used in the manufacture of copolymers according to the invention consists of olefins containing 2—6 carbon atoms. Preferably, ethylene or propylene is used, but olefins having a longer carbon chain, such as 1-butene, pentene and 1-hexene, may be used just as well.

The catalyst used is a metallocene-type catalyst. The metallocene may be a metallocene of any type. Thus, suitable metallocene compounds include compounds having the formula  $(Cp)_m R_n M R'_p X_p$ , where Cp is an unsubstituted or substituted and/or fused homo- or heterocyclopentadienyl, R is a group containing 1-4 carbon atoms and serving as a bridge between two Cp rings, M is a transition metal belonging to group 4A, 5A or 6A (Hubbard), R' is a  $C_1$ - $C_2$  hydrocarbyl or hydroxycarbyl group, and X is a halogen, m being 1—3, n being 0 or p being 0—3, and the sum  $m+n+p$  corresponding to the state of oxidation of the transition metal M. The transition metal is preferably zirconium or hafnium, most preferably zirconium. Examples of suitable metallocene compounds include bis(n-butylcyclopentadienyl) zirconium dichloride, 1,2-ethylene-bis(indenyl) zirconium dichloride, and 1,2-ethylene-bis(indenyl) hafnium dichloride.

The polymerization activity of the catalyst can also be increased by using activators such as alumoxane. One method is to add the alumoxane to the metallocene component either before, simultaneously or after the metallocene. Another method is to add the activator directly into the polymerization reactor.

Suitable activators include alumoxane compounds having the formula  $R-(Al(R)-O)_n-AlR_2$  or  $(-Al(R)-O)_m$ , where  $n$  is 1-40,  $m$  is 3-40, and  $R$  is a  $C_1-C_8$  alkyl group. Preferably  $R$  is a methyl group.

- 5 The support used may be any porous or inert support, such as silica or alumina or mixtures thereof.

The polymerization may be carried out by any method, for example by slurry polymerization or gas phase polymerization. Thus the polymerization may be carried  
10 out, for example, at a temperature of 60-100 °C and under a pressure of 1-100 bar. The partial pressure of olefin in the reactor may vary within the range 1-3 bar and the amount of comonomer within the range 0.5—10 mmol.

The invention is described below in greater detail, with reference to the accompany-  
15 ing examples.

### Materials

Bis(*n*-butylcyclopentadienyl) zirconium dichloride  $(n-butCp)_2ZrCl_2$ , dicyclopenta-  
20 dienyl zirconium dichloride  $Cp_2ZrCl_2$ , 1,2-ethylene-bis(indenyl) zirconium di-  
chloride  $Et(Ind)_2ZrCl_2$ , (dimethylsilyl-bis(1H-indenyl)) zirconium dichloride  
 $Me_2Si(Ind)_2ZrCl_2$  and methylalumoxane (MAO) were of a commercial grade and  
were not purified separately. Polymerization-grade ethylene and propylene and the  
n-heptane and toluene serving as the medium were purified by feeding them through  
25 a column series to eliminate any moisture and oxygen residues. The comonomer  
methyl-9-decenoate was of own production.

### Polymerization

30 Ethylene copolymerizations were carried out in a 0.5 dm<sup>3</sup> autoclave at a temperature  
of 60 °C for 40 minutes, and the reaction medium used was n-heptane.

The medium n-heptane (350 cm<sup>3</sup>) was fed into a vacuumized reactor, blanketed with nitrogen and equipped with a stirrer. The rotation velocity of the stirrer was constantly 400 rotations per minute. The comonomer was added in one batch under nitrogen blanket, and the cocatalyst MAO (Al/Zr = 3000 mol/mol) was added at the beginning of the polymerization by using a pump. After the polymerization temperature had been reached, ethylene was fed into the reactor. The consumption of ethylene was monitored by means of a mass flow controller. After equilibrium had been reached, polymerization was started by pumping the catalyst into the reactor. The partial pressure of ethylene or propylene was maintained constant (2.5 bar ethylene overpressure) by means of an electronic pressure controller and a solenoid valve, and the reactor temperature was maintained constant ( $\pm 0.1$  °C). The conversion was maintained low in order that it could be assumed that the concentration in the reactor remained constant. At 40 minutes, reactor pressure was released and the obtained polymer product was washed with a solution of ethanol and hydrochloric acid, and was dried.

Propylene copolymerizations were carried in the same manner as ethylene copolymerizations except that the medium used was toluene in an amount of 300 cm<sup>3</sup>, the polymerization time was 60 minutes and the polymerization temperature was 30 °C, and the propylene overpressure was 3.0 bar. The catalyst used was 1,2-ethylene-bis(indenyl) zirconium dichloride.

#### Characterization of the polymers

The compositions of the copolymers of ethylene and the functional monomer were determined by using a Jeol NMR spectrometer.

The melting points and enthalpies were determined from the peak of the DSC curve by using a Perkin Elmer DSC-7 instrument. The DSC measurements were carried out by reheating the sample to 180 °C at heating rates of 2 and 10 °C/min.

The molar masses and the molar mass distributions were measured using a Waters-type ALC/GPC 150 instrument in which there had been installed 3 TOSOH mixed-bed columns in which the polystyrene barrier limit was  $4 \times 10^8$  at a temperature of 135 °C. The solvent used was 1,2,4-trichlorobenzene having a flow rate of 1.0 ml/min.

### Examples

Ethylene was copolymerized with methyl-9-decenoate. The catalysts used were combinations (n-butCp)<sub>2</sub>ZrCl<sub>2</sub>/MAO, Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO, Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO and Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO. The polymerization conditions and some product properties are shown in Table 1.

Table 1

Ex. No.	Catalyst 2 mg	Comonomer amount mmol	Activity kg/g cat h	Molar mass $M_w \cdot 10^{-3}$	Mv/Mn	Tm °C
1	(n-butCp) <sub>2</sub> ZrCl <sub>2</sub>	1	5,0	98	3,1	131,5
2	"	2	4,1	139	3,8	134,5
3	"	3	2,1	131	3,9	134,0
* 4	"	4	0,2	60	5,2	133,3
5	Cp <sub>2</sub> ZrCl <sub>2</sub>	1	2,5	120	4,6	130,4
6	Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	1	1,9	265	4,8	130,8
7	Me <sub>2</sub> Si(Ind) <sub>2</sub> ZrCl <sub>2</sub>	1	1,1	104	2,9	128,1

polymerization temperature 60 °C

polymerization time 40 min

ethylene pressure 2.5 bar

Zr =  $4.94 \times 10^{-2}$  mol

Al (as MAO) =  $1.98 \times 10^{-2}$  mol

\* Composition of the ethylene copolymer



5	Comonomer	Comonomer feed mmol	In the copolymer	
			% wt.	molar %
	methyl-9-decenoate	4	1.1	0.2

10 Activity decreases as the amount of comonomer fed in increases.

Copolymerizations of propylene and methyl-9-decenoate were carried out by using the combination 1,2-ethylene-bis(indenyl) zirconium chloride/MAO. The polymerization conditions and some properties of the product are shown in Table 2.

15

**Table 2**

20	Ex. No.	Catalyst 2 mg	Comonomer amount mmol	Activity kg/g cat h	Molar mass $M_w \cdot 10^{-3}$	Mv/Mn	Tm °C
	8	Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	0,5	3,9	33	1,8	135,5

Al/Zr 4000 mol/mol

25 MAO solution 12.4 ml (7.0 cm) from burette

Propylene 3.0 bar

30 °C

300 ml (261 g) toluene

400 rpm

30 60 min

## Claims

1. An olefin copolymer prepared by polymerizing an olefin containing 2—5 carbon atoms with a monomer containing a functional group, **characterized** in that the functional monomer is 9-methyl decenoate.  
5
2. An olefin copolymer according to Claim 1, **characterized** in that the olefin has been selected from the group ethylene and propylene.
- 10 3. An olefin copolymer according to Claim 1—2, **characterized** in that it has been prepared by using a metallocene catalyst.
4. An olefin copolymer according to any of the above claims, **characterized** in that the metallocene is selected from the group bis(n-butylcyclopentadienyl) zirconium chloride (n-butCp)<sub>2</sub>ZrCl<sub>2</sub>, dicyclopentadienyl zirconium dichloride Cp<sub>2</sub>ZrCl<sub>2</sub>, 1,2-ethylene-bis(indenyl) zirconium dichloride Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, (dimethylsilyl-bis(1H-indenyl) zirconium dichloride Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>.  
15
5. An olefin copolymer according to Claim 4, **characterized** in that the polymerization has been carried out using methylalumoxane (MAO) as an activator.  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 96/00494

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 210/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, CAPLUS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0356692 A2 (DEMITSU KOSAN COMPANY LIMITED), 7 March 1990 (07.03.90), page 3, line 1 - line 21, claim 1  --	1-2
X	US 4523929 A (ILAN DUVDEVANI ET AL), 18 June 1985 (18.06.85), abstract; column 4, line 1 - line 35; example 1, line 15 - line 35  --	1-2
A	US 4518757 A (DONALD N. SCHULZ ET AL), 21 May 1985 (21.05.85), abstract, claims 1,3  -- -----	1-2

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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29 November 1996

Date of mailing of the international search report

10 -12- 1996

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**INTERNATIONAL SEARCH REPORT**  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE-D, T- 68911065	07/04/94
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